

# Direct generation of charge carriers in c-Si solar cells due to embedded nanoparticles

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## Abstract

It is known that silicon is an indirect band gap material, reducing its efficiency in photovoltaic applications. Using surface plasmons in metallic nanoparticles embedded in a solar cell has recently been proposed as a way to increase the efficiency of thin film silicon solar cells. The dipole mode that dominates the plasmons in small particles produces an electric field having Fourier components with all wave numbers. In this work, we show that such a field creates electron-hole-pairs without phonon assistance, and discuss the importance of this effect compared to radiation from the particle and losses due to heating.

## I. INTRODUCTION

Present day solar cell industry is completely dominated by the use of silicon as the active material. It's main advantages are availability, disposability and several decades of industrial metallurgical development, compared to the poisonous or rare elements of, e.g., GaAs. However, silicon is not an ideal material for solar cells. One disadvantage is that it has an indirect band gap. This means that photons with energy close to the band gap can only be absorbed in phonon-assisted processes. Therefore, the absorption of these photons is weak, and the silicon wafer can not be made too thin if one is to absorb this part of the solar spectrum. The material costs and limited production capacity for solar grade silicon mean that the thickness required in todays first generation solar cells is a significant obstacle to their commercial success. Also, due to the limited lifetime of the electron-hole pairs, thicker cells may suffer from larger recombination rate and reduced efficiency.

The question is thus how to increase the optical path lengths of near band gap photons inside the silicon, without increasing wafer thickness. Several approaches have been tried, including texturing of the wafer front or rear surface in various patterns and on different length scales. For length scales larger than the wave length, the incoming light is refracted into angles more parallel to the wafer.<sup>1</sup> For length scales close to or smaller than the wave-length, diffraction may couple light into guided modes.<sup>2</sup> However, the texturing will often lead to an increase in surface defect states and thereby increase recombination rates.

As an alternative to texturing, it has been proposed to place metallic nanoparticles near the surface of the wafer.<sup>3</sup> The nanoparticles scatter the incoming light through a surface plasmon resonance. Surface plasmons, or surface plasmon polaritons, are electron density fluctuations at the interface between a metal and a dielectric material. For a good introduction, see, e.g., Raether<sup>4</sup> for plasmons in general, and Bohren&Huffman<sup>5</sup> for plasmons on small particles. On the surface of nanoparticles, the plasmons can be excited by an incoming plane wave, and they exhibit a marked, tunable resonance. For frequencies near the resonance, nanoparticles have an optical cross section much larger than their geometrical cross section. If this resonance could be tuned to match the band gap of silicon, near bandgap photons could be absorbed into the plasmon state with high probability, while higher energy photons would be unaffected. Certain progress has already been made in the plasmon tuning, e.g., at the University of New South Wales,<sup>6,7</sup> but further development is required.

We believe that the energy of the surface plasmons can then be used to create electron-hole pairs in two ways. First, the energy can be emitted as light in directions along the wafer. This gives a longer optical path inside the wafer, and thereby increases the indirect absorption.<sup>6</sup>

Second, the near field of the nanoparticles can excite electron-hole pairs without phonon assistance, the momentum being transferred to the nanoparticle. This second process has to our knowledge not been considered in the literature, and is the subject of the present paper. Our results indicate that this mechanism will give an extra contribution to the electron-hole pair generation, compared to estimates that only take into account the re-radiation of power, increasing the relative benefit of introducing the nanoparticles.

Some of the plasmon energy goes into heating of the nanoparticles and is obviously lost. This loss should be compared with the losses due to the limited optical path when not exploiting the plasmons, or, if texturing is used to increase the optical path length, with increased losses due to recombination at interfaces. The plasmons will give an improved efficiency if the losses to heating are smaller than previous losses due to optical path length or recombinations. If the resonance is properly tuned, the only photons significantly affected will be those that would otherwise be lost. Any fraction of this near bandgap light that can be used efficiently contributes to a net gain for the cell.

For particles larger than the wavelength, a large fraction of the light will be reflected rather than excite plasmons.<sup>5</sup> We therefore consider only particles smaller than the wavelength of the incoming light. For such particles, the plasmons can be approximated by a dipole mode, corresponding to uniform polarization of the nanoparticle.<sup>5</sup> While the dipole approximation is usually only accepted for particles with diameter less than one tenth of a wavelength, we accept it as a first approximation for our order of magnitude estimates. We are not aware of any studies of how the near field is changed by an interface between the layer embedding nanoparticles and the active layer of the solar cell. For simplicity, we will therefore restrict the further discussion to the case of an electric dipole located inside an infinite medium consisting of silicon. The dipole is excited by an incoming plane wave.

The far-field energy radiated from the dipole represents the maximum energy that can be absorbed by indirect absorption. In real applications, some of this light will inevitably be lost. The presence of an interface may also increase the total emission,<sup>8,9</sup> but for the sake of our order of magnitude estimates, we will ignore this effect.

The goal of this paper is to demonstrate that the direct absorption effect should be considered when modeling the effect of plasmons, and that it may have important implications for the optimal sizing and positioning of the plasmons. The fact that plasmons can lead to an increase in efficiency has been experimentally verified.<sup>7,10</sup> We therefore focus on the *relative* importance of the two mechanisms that could contribute to the increase, and how this could influence cell design considerations.

## II. THEORY

We use classical electrodynamics to describe both the nanoparticles and the fields. The interaction with the silicon is described by perturbation theory, and we use the tight binding model and the parabolic approximation of the band gap extrema for the wave function of the silicon.

We consider the incoming light to have a frequency close to the band gap of silicon. This corresponds to  $\hbar\omega = 1.1$  eV, or  $\omega \approx 10^{15}$  s<sup>-1</sup>. We then get for the wavelength of this radiation  $\lambda = 2\pi c/\omega \approx 1$   $\mu\text{m}$ , and from  $c = \omega/k_p$  we get the photon wavenumber  $k_p \approx 6 \cdot 10^6$  m<sup>-1</sup>.

The vector potential due to a dipole is given as:<sup>11</sup>

$$\begin{aligned}\mathbf{A} &= \frac{i\omega\mu_0}{4\pi r} e^{-i(k_p r - \omega t)} \mathbf{p}_0 = i\mathbf{A}_0 A_r, \\ \mathbf{A}_0 &= \frac{\omega\mu_0 k_p p_0}{4\pi} \mathbf{e}_{\mathbf{p}}, \quad A_r = \frac{1}{k_p r} e^{-i(k_p r - \omega t)}\end{aligned}\tag{1}$$

where  $\mathbf{p}_0$  is the dipole moment, and  $p_0 = |\mathbf{p}_0|$ .  $r$  is the distance from the dipole. Using the previous rough estimates for  $\omega$  and  $k_p$  we get that  $A_0/p_0 \approx 10^{15}$  Js/C<sup>2</sup>m<sup>2</sup>, while  $A_r$  is a dimensionless function containing all spatial dependencies of  $\mathbf{A}$ . The magnitude of  $p_0$  will be addressed later, but is not necessary for the following comparisons of different terms. The scalar potential can be cast in the form  $\Phi_0\Phi_r$  where

$$\Phi_0 = \frac{k_p^2 p_0}{4\pi\epsilon_0}, \quad \Phi_r = \frac{\cos\theta}{k_p r} \left(i + \frac{1}{k_p r}\right) e^{-i(k_p r - \omega t)},\tag{2}$$

$\theta$  is the angle from the dipole axis. We can estimate  $\Phi_0/p_0 \approx 3 \cdot 10^{23}$  J/C<sup>2</sup>m, while  $\Phi_r$  is again dimensionless.

The Hamiltonian of the system is:<sup>12</sup>

$$H = \frac{(-i\hbar\nabla + e\mathbf{A})^2}{2m} - e\Phi\tag{3}$$

$$= -\frac{\hbar^2 \nabla^2}{2m} - \frac{ie\hbar(\nabla \cdot \mathbf{A} + \mathbf{A} \cdot \nabla)}{2m} + \frac{e^2 \mathbf{A}^2}{2m} - e\Phi \quad (4)$$

where  $e$  is the positive elementary charge. The  $\mathbf{A}^2$ -term can safely be neglected. Using the Lorentz gauge,  $\nabla \cdot \mathbf{A} + c^2 \dot{\Phi} = 0$ , where  $c = (\epsilon_0 \mu_0)^{1/2}$ , we rewrite the interaction Hamiltonian as

$$\begin{aligned} H_{\text{int}} &= A_r \mathbf{C}_a \cdot \nabla - \Phi_r C_b; \\ \mathbf{C}_a &= 2\mu_B \mathbf{A}_0, \quad C_b = \left(1 + \frac{\hbar\omega}{2mc^2}\right) e\Phi_0 \end{aligned} \quad (5)$$

where  $\mu_B$  is the Bohr magneton. Since  $mc^2 \gg \hbar\omega$ ,  $C_b \approx e\Phi_0$ .

For the wave function, we use the standard tight binding approximation,<sup>13</sup> writing the wave function as

$$\Psi_{\mathbf{k}}(r) = e^{i\mathbf{k} \cdot \mathbf{r}} \frac{1}{\sqrt{N_a}} \sum_n \sum_l b_{\mathbf{kl}} \Psi_{nl}(r) \quad (6)$$

where  $\Psi_{nl}(r) = \Psi_l(r - \mathbf{R}_n)$  is the  $l$ -th orbital corresponding to the atomic wave function centered at the  $n$ -th atom located at  $\mathbf{R}_n$ . The parameters  $b_{\mathbf{kl}}$  can in principle be found for each point in  $k$ -space. For states at the valence band maximum, there seems to be good agreement between theory and experiment. For the conduction band minimum, the fitting parameters are still optimized either for the position in  $k$ -space or for the effective mass in different directions, depending on what is considered the most important. Based on Klimeck *et al.*<sup>14,15</sup> we still assume that the minimum can be described by a combination of single electron  $p$ ,  $s$  and  $s^*$  states, where  $s^*$  is an excited  $s$ -state.

The transition rate for each  $\mathbf{k}'$ ,  $\mathbf{k}$  can then be found using Fermi's golden rule,

$$W_{\mathbf{k}'\mathbf{k}} = \frac{2\pi}{\hbar} |\langle \mathbf{k}' | H_{\text{int}} | \mathbf{k} \rangle|^2 \delta(E_{\mathbf{k}'} - E_{\mathbf{k}} - \hbar\omega) \quad (7)$$

where  $\mathbf{k}'$  denotes the final state, and  $\mathbf{k}$  the initial one. In the following calculations, we will assume that the final state is near the conduction band minimum. There are six equivalent such minima, the effect of this will be addressed later. The absorbed energy by direct pair creation is given as  $P_d = \sum_{\mathbf{k}', \mathbf{k}} \hbar\omega W_{\mathbf{k}'\mathbf{k}}$ . We calculate this using the parabolic approximation that is valid close to the band edges. Since we are interested in initial states close to the top of the valence band and final states close to a minimum in the conduction band one can assume that the interaction matrix element is weakly dependent on  $\mathbf{k}$  and  $\mathbf{k}'$ ,  $W_{\mathbf{k}'\mathbf{k}} \approx W_{\mathbf{k}_0\mathbf{0}}$ .

Writing  $\mathbf{k}'' = \mathbf{k}' - \mathbf{k}_0$  we get

$$E_{\mathbf{k}'} = E_g + \frac{\hbar^2 \mathbf{k}''^2}{2m_c}, \quad E_{\mathbf{k}} = -\frac{\hbar^2 \mathbf{k}^2}{2m_v}, \quad (8)$$

and using

$$\sum_{\mathbf{k}} = V \int d^3\mathbf{k} \frac{1}{(2\pi)^3} = \frac{4\pi V}{(2\pi)^3} \int k^2 \frac{dk}{dE} dE \quad (9)$$

this gives

$$\sum_k W_{\mathbf{k}'\mathbf{k}} \delta(E_f - E_i - \hbar\omega) \quad (10)$$

$$\begin{aligned} &= W_{\mathbf{k}_0\mathbf{0}} \frac{2^5 \pi^2 V^2}{(2\pi)^6 \hbar^6} (m_c m_v)^{\frac{3}{2}} \times \\ &\quad \int_{E_g}^{\infty} dE_f \int_0^{\infty} -dE_i \sqrt{(E_f - E_g)(-E_i)} \delta(E_f - E_i - \hbar\omega) \\ &= W_{\mathbf{k}_0\mathbf{0}} \frac{V^2 (m_c m_v)^{\frac{3}{2}}}{2^4 \pi^3 \hbar^6} (\hbar\omega - E_g)^2 \end{aligned} \quad (11)$$

where  $m_c, m_v$  are the effective masses of the valence and conduction bands, respectively, and  $E_g$  is the gap energy.

Note that the energy dependence of the absorption is the same as that of indirect absorption, rather than that for direct absorption in direct band gap semiconductors, for which it is proportional to  $(\hbar\omega - E_g)^{1/2}$ . The reason for this is the spread of Fourier components in the dipole field, which take the role of the spread in phonon wave numbers in the case of indirect absorption.

### III. CALCULATIONS

We term the power emitted as radiation  $P_r$ , the power lost to heating  $P_h$ , and the power going into direct electron-hole pair generation  $P_d$ .

After standard calculations we get the absorption:

$$\begin{aligned} P_d &= \frac{2(m_c m_v)^{\frac{3}{2}} \omega (\hbar\omega - E_g)^2}{\hbar^6 k_p^2} \left| \sum_{l'l} b_{\mathbf{k}'l'} b_{\mathbf{k}l} \left\{ \frac{\alpha_{\mathbf{k}'\mathbf{k}} (\langle l' | \mathbf{C}_a \cdot \nabla | l \rangle + i \mathbf{C}_a \cdot \mathbf{k})}{(|\mathbf{k}' - \mathbf{k}|^2 - k_p^2)} + \frac{i \beta_{\mathbf{k}'\mathbf{k}} C_b \langle l' | l \rangle}{|\mathbf{k}' - \mathbf{k}|} \right\} \right|^2 ; \\ \alpha_{\mathbf{k}'\mathbf{k}} &= \cos(|\mathbf{k}' - \mathbf{k}| r_a) + \frac{i k_p}{|\mathbf{k}' - \mathbf{k}|} \sin(|\mathbf{k}' - \mathbf{k}| r_a) , \\ \beta_{\mathbf{k}'\mathbf{k}} &= \left\{ \frac{k_p \cos(|\mathbf{k}' - \mathbf{k}| r_a) + i |\mathbf{k}' - \mathbf{k}| \sin(|\mathbf{k}' - \mathbf{k}| r_a)}{|\mathbf{k}' - \mathbf{k}|^2 - k_p^2} + \frac{\sin(|\mathbf{k}' - \mathbf{k}| r_a)}{|\mathbf{k}' - \mathbf{k}| k_p r_a} \right\} . \end{aligned} \quad (12)$$

Here  $r_a$  is the radius of the grain.  $\langle l' | \mathcal{O} | l \rangle = \int \Psi_{l'}^* \mathcal{O} \Psi_l d^3r$  denotes integration over the atomic orbitals for the operator  $\mathcal{O}$ . It can be assumed that the elements of the sum where  $n' \neq n$  will only give small corrections.

Writing  $\mathbf{p}_0 \cdot \nabla = \sum_{i=x,y,z} \mathbf{e}_i p_i \nabla_i$ , and having an initial state that is a combination of  $p$ -states, only the matrix elements  $\langle s | e_i p_i \nabla_i | p_i \rangle$  do not vanish. They are expected to be of the order of  $1/a$  where  $a$  is the lattice constant,  $5.4 \cdot 10^{-10}$  m for crystalline silicon. Regarding the contributions of the scalar field and Umklapp processes, only the elements with  $l = l'$  do not vanish.

While each of the  $x, y, z$  give different contributions depending on the orientation of the dipole, it should be noted that there exist six equivalent minima in the conduction band. While the matrix element due to one minimum will be non-isotropic, the sum over all six minima is expected to be isotropic and equivalent to two minima with  $\mathbf{p}_0 \parallel \mathbf{k}$ . We define  $k_0 = |\mathbf{k}' - \mathbf{k}|$ . At the minima we have  $k_0 \approx 0.85 \cdot 2\pi/a \approx 10^{10} \text{m}^{-1}$ .

We see that all terms in Eq. 12 show oscillations with period  $1/|\mathbf{k}' - \mathbf{k}|$  with increasing nanoparticle radius. As the nanoparticle diameter cannot be expected to be well defined on this length scale (atomic radius), we will simply take the average over one period. We believe this to be justified both from considering the limited coherence length of the electrons, and from the fact that any physical measurement would include a dispersion of particle sizes. While the limit of  $r_a \rightarrow 0$  is mathematically well defined, it is not physically meaningful, as it describes a nanoparticle with less than one atom.

Interestingly, the scalar potential provides much larger contribution than the vector potential. Keeping only the largest terms, we can make an order of magnitude estimate,

$$P_d \approx \frac{(m_c m_v)^{\frac{3}{2}} \omega e^2 p_0^2}{32 \pi^2 \hbar^6 k_0^4 \epsilon_0^2} \Delta E^2 (k_p + r_a^{-1})^2 \quad (13)$$

$P_d$ ,  $P_r$  and  $P_h$  are all proportional to  $p_0^2$ . We define the damping coefficients  $\gamma_d = P_d/p_0^2$ ,  $\gamma_r = P_r/p_0^2$ ,  $\gamma_h = P_h/p_0^2$  and  $\gamma = \gamma_d + \gamma_r + \gamma_h$ . We use these coefficients when comparing the importance of the different mechanisms. To find the total absorbed power, we also need to estimate the dipole moment,  $p_0$ , which is determined by the amplitude of the incident wave,  $E_0$ , and the polarizability of the nanoparticles,  $\alpha$ , as  $p_0 = \alpha(\omega) E_0$ . While the polarizability is in general dependent on the particle volume and shape, at the plasmon resonance it is determined by the damping only. This can be shown from equating the power absorbed from a plane wave by an oscillating dipole,  $E_0 p_0 \omega / 2$ , with the total emitted power,  $\gamma p_0^2$ , giving

$$\alpha = \frac{\omega}{2\gamma(\omega)}. \quad (14)$$

Assuming that the incident light is absorbed by a layer of nanoparticles with a 2D density  $n$ , we get

$$\begin{aligned} \frac{P_d}{W} &\approx \frac{n(m_c m_v)^{3/2} \omega (\hbar\omega - E_g)^2 e^2 \alpha^2}{16\pi^2 \hbar^6 c k_0^4 \epsilon_0^3} (k_p + r_a^{-1})^2 \\ &\propto \frac{\gamma_d}{(\gamma_d + \gamma_r + \gamma_h)^2}. \end{aligned} \quad (15)$$

Here  $W = \epsilon_0 E_0^2 c / 2$  is the incident power per area. As long as  $\gamma_d$  is small compared to  $\gamma_r + \gamma_h$ , it will not significantly change the polarizability, but if it becomes of the same order, the decrease in polarizability will be more important than the increase in absorption. This can easily be remedied by a higher density of nanoparticles, but if the density becomes very high, interaction between neighboring particles will change both the polarizability and the plasmon resonance frequency.

#### IV. RESULTS

We see that the direct absorption is proportional to  $(\Delta E)^2 \equiv (\hbar\omega - E_g)^2$ , the excess energy after bridging the band gap, squared. This is the same energy dependence as found for indirect absorption if the single phonon processes including emission or absorption of a phonon are considered separately.

The resonance of the nanoparticles has a certain width, so  $\Delta E$  also has a spread. To get a feeling for the order of magnitude of  $P_d$  we define  $x = \Delta E / \hbar\omega$  and express the results through this. We are interested in frequencies where direct absorption of a plane wave would be impossible, so an  $x$  of close to one is irrelevant. The direct absorption shows no explicit dependence on temperature, as opposed to indirect absorption. This may indicate a method for differentiating between direct and indirect absorption in solar cells containing nanoparticles. The possibility of changes in the band structure of silicon with temperature should still be considered.

The direct absorption,  $P_d$ , should be compared with the energy lost to heating,  $P_h$  or by radiation,  $P_r$ . From Eq. (12) we have

$$P_d = \gamma_d p_0^2, \quad \gamma_d \approx 3 \cdot 10^{44} x^2 \left(1 + \frac{1}{(k_p r_a)}\right)^2 \frac{\text{J}}{\text{sm}^2 \text{C}^2}, \quad (16)$$

where  $x$  will usually be significantly less than one. With 50 nm particle radius we get  $k_p r_a \approx 0.3$ . The total integrated radiation from a dipole with the same dipole moment,  $p_0$



is:<sup>11</sup>

$$P_r = \frac{c}{12\pi\epsilon} \frac{p_0^2 (2\pi)^4}{\lambda^4} = \gamma_r p_0^2. \quad (17)$$

Using that  $k_p \lambda = 2\pi$  we obtain

$$\gamma_r = \frac{ck_p^4}{12\pi\epsilon} \approx 10^{44} \frac{\text{J}}{\text{sm}^2\text{C}^2} \quad (18)$$

giving

$$\frac{\gamma_d}{\gamma_r} \approx 3x^2 \left( 1 + \frac{1}{(k_p r_a)^2} \right). \quad (19)$$

As shown in figure 1, we see that for sufficiently small particles and if  $x$  is not too small,  $\gamma_d$  can be of the same magnitude as  $\gamma_r$ , or even larger. However, the gain for small particles requires that the particle is very close to the silicon. Designs where the nanoparticles are located outside the silicon may lose the benefit of the  $1/k_p r_a$  term.

In the previously mentioned experiments, the nanoparticles were located close to a thin silicon wafer. For dipoles located at such an interface, the total radiation increases, and a large fraction of the radiation is directed into guided modes in the silicon wafer.<sup>3,6,8,9</sup> For the light in the bound modes, it is assumed that the optical path length is sufficient to allow most of the radiation to be absorbed in indirect electron hole pair creations. At the same time the areas where the near field is strongest, has no silicon to absorb the energy. Under such circumstances, it should be assumed that  $\gamma_r$  dominates  $\gamma_d$ .

However, there is also a possibility that radiated energy can excite a plasmon on a neighboring particle, then again to be reemitted. This would reduce the positive contribution of the plasmons in architectures where the radiation along the wafer is exploited, as more energy would be lost to heat. If we instead place the nanoparticles inside the silicon and exploit the direct absorption, less energy would be reabsorbed by neighboring nanoparticles, and thereby less would be lost to heat.

Using a simple resistivity argument,  $\gamma_h$  can be estimated as

$$\gamma_h \approx \frac{3\omega^2 \rho}{4\pi r_a^3} \approx 2 \cdot 10^{42} \frac{1}{(k_p r_a)^3} \frac{\text{J}}{\text{sm}^2\text{C}^2} \quad (20)$$

for silver. For small particles, heating will take over as the dominant damping mechanism, as shown in figure 1.

## V. CONCLUSIONS

Our findings indicate that direct absorption due to surface plasmons on metal nanoparticles does occur, and may give important corrections to the total absorption for realistic parameters.

The direct absorption has been found to be

- proportional  $\Delta E^2 = (\hbar\omega - E_g)^2$ ;
- independent of temperature;
- inversely proportional to the k-space position of the conduction band gap minimum to the fourth power;
- comparable in magnitude to radiated energy in some cases.

The existence of the direct absorption mechanism is an argument for placing the nanoparticles inside the silicon, rather than in front of, or at the rear of the cell. This gives the additional requirement that the problem of recombination centers at the particle surface can be kept to a minimum.

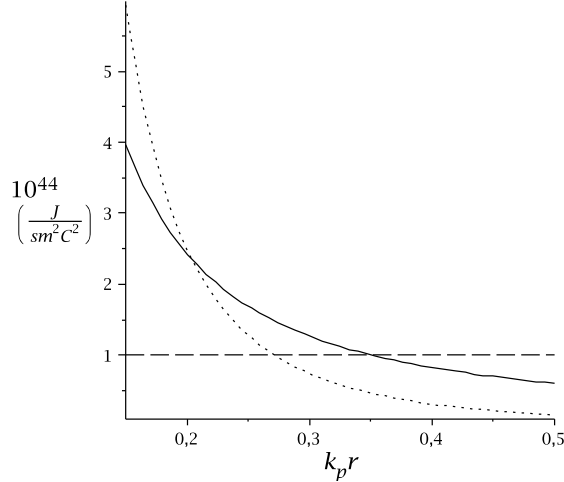


FIG. 1: The three damping mechanisms as function of  $k_p r$ . For small  $k_p r$ ,  $\gamma_h$  dominates (dotted line), for large  $k_p r$ ,  $\gamma_r$  dominates (dashed line), while  $\gamma_d$  (solid line) may dominate in the middle region if  $x$  is sufficiently large (here for  $x = 0.15$ )

Ideally, the size of the nanoparticles should be so small that  $\gamma_d$  dominates  $\gamma_r$ , but not so small that heating takes over as the dominant mechanism. We assume that diameters from about a tenth to half a wavelength could be suitable, depending on the conductivity of the nanoparticle. The plasmon resonance should be tuned using choice of material and particle shape (flattened for red-shift<sup>5</sup>), to match the band gap of silicon.

The main questions that remain unanswered in our study concern the effects of interfaces and surface states for the direct absorption. We have not considered how an interface changes the near field, and the presence of surface states in the silicon may significantly change the problem in unpredictable ways. As the main contribution is from very near the dipole, both surface electron states and the alteration of the field due to an interface may be very important. There are also some unaddressed problems related to the averaging over particle radii and the finite coherence length of the electrons in the silicon.

It is possible that higher order modes will give larger contributions to the absorption, these modes have been shown to be significant for nanoparticles of sizes where reradiation is larger than heating.

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- <sup>1</sup> P. Campbell, M. A. Green, *Journal of Applied Physics* **62**, No. 1, Jul. 1, 1987, 243-249.
- <sup>2</sup> P. Sheng, A. N. Bloch and R. S. Stepleman, *Applied Physics Letters* **43** (6), 579,(1983)
- <sup>3</sup> K. R. Catchpole and S. Pillai, *Journal of Applied Physics* **100**, 044504 (2006).
- <sup>4</sup> H. Raether, *Surface Plasmons on Smooth and Rough Surfaces and on Gratings*, Springer-Verlag (1988).
- <sup>5</sup> C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles*, John Wiley & Sons (1984).
- <sup>6</sup> S. Pillai, K. R. Catchpole, T. Trupke, G. Zhang, J. Zhao and M. A. Green, *Applied Physics Letters* **88**, 161102 (2006).
- <sup>7</sup> S. Pillai, K. R. Catchpole, T. Trupke, M. A. Green, *Journal of Applied Physics* **101**, 093105 (2007).
- <sup>8</sup> J. Mertz, *J. Opt. Soc. Am. B* **17**, No. 11/November 2000
- <sup>9</sup> H. Benisty, R. Stanley, M. Mayer, *J. Opt. Soc. Am. A* **15** No. 5/May 1998.
- <sup>10</sup> D. Derkacs, S. H. Lim, P. Matheu, W. Mar, E. T. Yu, *Applied Physics Letters* **89**, 093103 (2006).
- <sup>11</sup> P. Lorrain and D. Carson, *Electromagnetic Fields and Waves*, Freeman 1970.
- <sup>12</sup> L. D. Landau and E. M. Lifshitz *Quantum Mechanics* (Butterworth-Heinemann 2002).
- <sup>13</sup> J. Singh *Physics of Semiconductors and their Heterostructures* McGraw-Hill (1993).
- <sup>14</sup> G. Klimeck, R. C. Bowen, T. B. Boykin, C. Salazar-Lazaro, T. A. Cwik, A. Stoica, *Superlattices and Microstructures*, **27**, 77 (2000).
- <sup>15</sup> A. S. Martins, T. B. Boykin, G. Klimeck, B. Koiller, *Phys. Rev. B* **72** 193204 (2005).
- <sup>16</sup> J. Nelson *The Physics of Solar Cells* (Imperial College Press 2003).
- <sup>17</sup> P. Würfel *Physics of Solar Cells* (Wiley-VCH 2005).